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(54) Improvements in or relating to zirconium alloys.

(57) Alpha zirconium alloy fabrication methods and resultant products exhibiting improved high temperature, high pressure steam corrosion resistance. The process, according to one aspect of this invention, utilizes a high energy beam thermal treatment to provide a layer of beta treated microstructure on an alpha zirconium alloy intermediate product. The treated product is then alpha worked to final size. According to another aspect of the invention, high energy beam thermal treatment is used to produce an alpha annealed microstructure in a Zircaloy alloy intermediate size or final size component. The resultant products are suitable for use in pressurized water and boiling water reactors.

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to the Zircaloy-2 alloy composition as taught in U.S. Patent No. 3,097,094. In addition oxygen is sometimes considered as an alloying element rather than an impurity, since it is a solid solution strengthener of zirconium.

Nuclear grade Zircaloy-2 or Zircaloy-4 alloys are made by repeated vacuum consumable electrode melting to produce a final ingot having a diameter typically between about 16 and 25 inches. The ingot is then conditioned to remove surface contamination, heated into the beta, alpha + beta phase or high temperature alpha phase and then worked to some intermediate sized and shaped billet. This primary ingot breakdown may be performed by forging, rolling, extruding or combinations of these methods. The intermediate billet is then beta solution treated by heating above the alpha + beta/beta transus temperature and then held in the beta phase for a specified period of time and then quenched in water. After this step it is further thermomechanically worked to a final desired shape at a temperature typically below the alpha/ alpha + beta transus temperature.

For Zircaloy alloy material that is to be used as tubular cladding for fuel pellets, the intermediate billet may be beta treated by heating to approximately 1050°C and subsequently water quenched to a temperature below the alpha + beta to alpha transus temperature. This beta treatment serves to improve the chemical homogeneity of the billet and also produces a more isotropic texture in the material.

Depending upon the size and shape of the intermediate product at this stage of fabrication, the billet may first be alpha worked by heating it to about 750°C and then forging the hot billet to a size and shape appropriate for extrusion. Once it has attained the desired size and shape (substantially round cross-section), the billet is prepared for extrusion. This preparation includes drilling an axial hole along the center line of the billet, machining the outside diameter to desired dimen-

tial direction in the alpha matrix and helps to provide the required creep and tensile properties in the circumferential direction.

The alpha matrix itself may be characterized by a heavily cold worked or dislocated structure, a partially recrystallized structure or a fully recrystallized structure, depending upon the type of final anneal given the material.

Where final material of a rectangular cross section is desired, the intermediate billet may be processed substantially as described above, with the exception that the reductions after the beta solution treating process are typically performed by hot, warm and/or cold rolling the material at a temperature within the alpha phase or just above the alpha to alpha plus beta transus temperature. Alpha phase hot forging may also be performed. Examples of such processing techniques are described in U.S. Patent Specification No. 3,645,800.

It has been reported that various properties of Zircaloy alloy components can be improved if beta treating is performed on the final size product or near final size product, in addition to the conventional beta treatment that occurs early in the processing. Examples of such reports are as follows: United States Patent Specification No. 3,865,635, United States Patent Specification No. 4,238,251 and United States Patent Specification No. 4,279,667. Included among these reports is the report that good Zircaloy-4 alloy corrosion properties in high temperature steam environments can be achieved by retention of at least a substantial portion of the precipitate distribution in two dimensional arrays, especially in the alpha phase grain boundaries of the beta treated microstructure. This configuration of precipitates is quite distinct from the substantially random array of precipitates normally observed in alpha worked (i.e. below approximately 1450°F) Zircaloy alloy final product where the beta treatment, if any, occurred much earlier in the

In accordance with one aspect of the present invention it has been found that the high temperature steam corrosion resistance of an alpha zirconium alloy body can be significantly improved by rapidly scanning the surface of the body with a high energy beam so as to cause at least partial recrystallization or partial dissolution of at least a portion of the precipitates.

Preferably the high energy beam employed is a laser beam and the alloys treated are selected from the groups of Zircaloy-2 alloys, Zircaloy-4 alloys and zirconium-niobium alloys. These materials are preferably in a cold worked condition at the time of treatment by the high energy beam and may also be further cold worked subsequently.

In accordance with the present invention intermediate as well as final products having the microstructures resulting from the above high energy beam rapid scanning treatments are also a subject of the present invention and include, cylindrical, tubular, and rectangular cross-section material.

In accordance with a second aspect of the present invention the high temperature, high pressure steam corrosion resistance of an alpha zirconium alloy body can also be improved by beta treating a first layer of the body which is beneath and adjacent to a first surface of said body so as to produce a Widmanstatten grain structure with two dimensional linear arrays of precipitates at the platelet boundaries in this first layer, while also forming a second layer containing alpha recrystallized grains beneath the first layer. The material so treated is then cold worked in one or more steps to final size, with intermediate alpha anneals between cold working steps.

Preferably any intermediate alpha or final alpha anneals performed after high energy beam beta treatment are performed at a temperature below approximately 600°C to minimize precipitate coarsening. It has been found that Zircaloy bodies surface beta treated in accordance

Figure 5 shows optical and scanning electron microscope micrographs of typical microstructures present in the as-laser treated tube.

In one embodiment of the present invention it was found that scanning of final size Zircaloy-4 tubing by a high power laser beam would provide high temperature, high pressure steam corrosion resistance even though a Widmanstatten basket-weave microstructure was not achieved. It was found that material processed as described in the following examples could achieve high temperature, high pressure steam corrosion resistance even though optical metallographic examination of the material revealed it to have partially or fully recrystallized microstructural regions with a substantially uniform precipitate distribution typical of that observed in conventionally alpha worked and annealed Zircaloy tubing.

The laser treatments utilized in this illustration of the present invention are shown in Table I. In all cases a 10.6 μ wavelength, 5 kilowatt laser beam was rastered over an area of 0.2 in. x 0.4 in. (0.508 cm x 1.08 cm) of conventionally fabricated, stress relief annealed, final size Zircaloy-4 tubing, the tubing having a mechanically polished (400-600 grit) outer surface, was simultaneously rotated and translated through the beam area under the conditions shown in Table I. As the tube rotation and tube withdrawal rates decreased, more energy was transmitted to the specimen surface and higher temperatures were attained. This relationship of tube speed to energy is illustrated by the increase in specific surface energy (that is energy striking a square centimeter of the tube surface) with decreasing tube rotation and tube withdrawal rates as shown in Table I. Although the treatment chamber was purged with argon at a rate of about 150 cubic feet/hour, most tubes were covered with a very light oxide coating upon exit from the chamber.

Representative sections of each treatment condition were metallographically polished to identify any

tubing generally had lower weight gains than the beta treated Zircaloy-4 control coupons. For comparison, conventionally processed cladding disintegrates after 5-10 days in the corrosion environment utilized.

Because beta-treated Zircaloy-4 with a Widmanstatten microstructure has good corrosion resistance in 454°C steam, it was anticipated, on the basis of optical metallography, that the laser treated specimens with the Widmanstatten structure (Figure 3) would also have good corrosion resistance. However, the change from catastrophic corrosion behavior to excellent corrosion behavior that occurred between rotation rates of 332 rpm and 285 rpm was not expected on the basis of optical metallography and forms the basis of this embodiment of the present invention. In order to determine what specific microstructural changes were responsible for this phenomena, transmission electron microscopy (TEM) samples were prepared from the 332-241 rpm tubing. The structures that are characteristic of these specimens are shown in Figures 4A and 4B. (The dark particles shown in these micrographs are not indigenous precipitates, but are oxides and hydride artifacts introduced during TEM specimen preparation.) All of the samples had areas which were well polygonized (Figures 4A, area X) and/or recrystallized (Figure 4B). The structures were quite similar, in overall appearance, to cold-worked Zircaloy-4 that had been subjected to a relatively severe stress relief anneal. Precipitate structures were typical of those in normally processed Zircaloy-4 tubing, although many precipitates were more electron transparent than normally expected, indicating that partial dissolution may have occurred. No qualitatively discernible difference between the specimens which had poor corrosion resistance and good corrosion resistance was noted. It is however theorized that dissolution of intermetallic compounds may result in enrichment of the matrix in Fe and/or Cr, thereby leading to the improved corrosion resistance observed.

In other embodiments of the present invention conventionally processed Zircaloy-2 and Zircaloy-4 tubes are scanned with a high energy laser beam which beta treats a first layer of tube material beneath and adjacent to the outer circumferential surface, producing a Widmanstatten grain and precipitate morphology in this layer while forming a second layer of alpha recrystallized material beneath this first layer (see Figure 5) . The treated tubes are then cold worked to final size and have been found to have excellent high temperature, high pressure steam corrosion resistance. The following examples are provided to more fully illustrate the processes and products in accordance with these embodiments of the present invention.

Note, as used in this application, the term scanning refers to relative motion between the beam and the workpiece, and either the beam or the workpiece may be actually moving. In all the examples the workpiece is moved past a stationary beam.

The laser surface treatments utilized in these illustrations of the present invention are shown in Table IV. In all cases a continuous wave CO_2 laser emitting a 10.6 μ wavelength, 12 kilowatt laser beam was utilized. An annular beam was substantially focused onto the outer diameter surface of the tubing and irradiated an arc encompassing about 330° of the tube circumference. The materials were scanned by the laser by moving the tubes through the ring-like beam. While being treated in a chamber continually being purged with argon, the tubes were rotated at a speed of approximately 1500 revolutions per minute while also being translated at the various speeds shown in inches per minute (IPM) in Table IV, so as to attain laser scanning of the entire tube O.D. surface. The variation in translation speeds or withdrawal or scanning speeds were used to provide the various levels of incident specific surface energy (in joules/centimeter squared) shown in Table IV. Under predetermined condi-

high pressure steam and the data are as shown in Tables VI and VII. It will be noted that in all cases the samples processed in accordance with this invention had significantly lower weight gains than the conventionally alpha worked material included in the test standards. It was noted, however, that in some cases varying degrees of accelerated corrosion were observed on the laser beta treated and cold worked samples (see Table VI 1120°C, and 1270-1320°C materials). These are believed to be an artifact of the experimental tube handling system used to move the tube under the laser beam which allowed some portions of tubes to vibrate excessively while being laser treated. These vibrations are believed to have caused portions of the tube to be improperly beta treated resulting in a high variability in the thickness of the beta treated layer of around the tube circumference in the affected tube sections, causing the observed localized areas of high corrosion. It is therefore believed that these incidents of accelerated corrosion are not inherent products of the present invention, which typically produces excellent corrosion resistance.

Oxide film thickness measurements performed on the corrosion-tested laser-treated and cold-worked Zircaloy-4 samples from the tests represented in Table VI surprisingly indicated that the inside diameter surface, as well as the outside diameter surface, both had equivalent corrosion rates. This was true for all the treatments represented in Table VI except for the 1120°C treatment, where the inner wall surface had a thicker oxide film than the outer wall surface.

Based on the preceding high temperature, high pressure steam corrosion tests it is believed that these alpha Zirconium alloys will also have improved corrosion resistance in PWR and BWR environments.

The mechanical property characteristics and hydriding characteristics of the treated materials were found to be acceptable.

TABLE I

LASER PROCESSING PARAMETERS FOR HEAT TREATMENT OF FINISHED DIMENSION ZIRCALOY TUBING

Condition No.	Tube Dimensions (dia/wall)	Beam Configuration (Line Source)*	Laser Power (on work)	Tube Rotation RPM/IPM**	Tube Withdrawal IPM	Power Density KW/cm^2	Calculated Incident Specific Surface Energy J/cm^2
1	0.375"/0.022"	0.2" x 0.4"	5 KW	485/590	146	9.7	197
2	0.375"/0.022"	0.2" x 0.4"	5 KW	473/574	142	9.7	202
3	0.375"/0.022"	0.2" x 0.4"	5 KW	455/552	137	9.7	210
4	0.375"/0.022"	0.2" x 0.4"	5 KW	430/521	129	9.7	223
5	0.375"/0.022"	0.2" x 0.4"	5 KW	407/494	122	9.7	235
6	0.375"/0.022"	0.2" x 0.4"	5 KW	376/456	113	9.7	254
7	0.375"/0.022"	0.2" x 0.4"	5 KW	332/403	100	9.7	288
8	0.375"/0.022"	0.2" x 0.4"	5 KW	285/345	86	9.7	336
9	0.375"/0.022"	0.2" x 0.4"	5 KW	241/293	72	9.7	390
10	0.375"/0.022"	0.2" x 0.4"	5 KW	196/238	59	9.7	488
11	0.375"/0.022"	0.2" x 0.4"	5 KW	147/178	44	9.7	651

*Major dimension of beam (0.4") aligned parallel to rotational axis of tube.

**IPM = inches per minute = vector sum of the rotational velocity and translational velocity (tube withdrawal IPM).

TABLE IV

LASER PROCESSING PARAMETERS FOR HEAT TREATMENT OF INTERMEDIATE DIMENSION ZIRCALOY TUBING

Run No.	Tube Dimensions (dia/wall)	Beam Configuration (Line Source)	Laser Power (on work)	Tube Rotation RPM	Tube Withdrawal IPM	Power Density KW/cm^2	Calculated Incident Specific Surface Energy J/cm^2	Estimated Maximum Surface Temp.
23	(Zr-4) 0.700/0.070	0.7" x 0.1"	12 KW	~1500	20	8.5	2550	~1210°C
24	"	"	"	"	"	"	"	
25	"	"	"	"	"	"	"	
26	"	"	"	"	"	"	"	
27	"	"	"	"	"	"	"	
28	"	"	"	"	"	"	"	
29	0.700/0.070	0.7" x 0.1"	12 KW	~1500	24	8.5	2125	~1150°C
30	"	"	"	"	"	"	"	
31	"	"	"	"	"	"	"	
32	"	"	"	"	"	"	"	
33	"	"	"	"	"	"	"	
34	0.700/0.070	0.7" x 0.1"	12 KW	~1500	28	8.5	1820	~1120°C
35	"	"	"	"	"	"	"	
36	"	"	"	"	"	"	"	
37	"	"	"	"	"	"	"	
44	"	"	"	"	29	"	1759	~1270-1320°C
45	"	"	"	"	29	"	1759	
46	"	"	"	"	31	"	1645	
42	0.700/0.070	0.7" x 0.1"	12 KW	~1500	32	8.5	1594	~1230°C
47	"	"	"	"	31	"	1645	
48	"	"	"	"	33	"	1545	

TABLE V

INGOT CHEMISTRY OF ZIRCALOY TUBES PROCESSED IN ACCORDANCE WITH THE INVENTION

	Zircaloy-4 Heat A Run Nos. 23-43	Zircaloy-4 Heat B Run Nos. 44-48	Zircaloy-2 Run Nos. 49-63
Sn	1.46-1.47 w/o	1.42-1.52 w/o	1.44-1.63 w/o
Fe	.22-.23 w/o	.19-.23 w/o	.14-.16 w/o
Cr	.11-.12 w/o	.10-.12 w/o	.11-.12 w/o
Ni	50 ppm	35 ppm	.05-.06 w/o
Al	42-46 ppm	39-58 ppm	35 ppm
B	0.5 ppm	0.25 ppm	0.2 ppm
Ca	NR	15 ppm	NR
Cd	0.5 ppm	0.25 ppm	0.2 ppm
C	115-127 ppm	125-165 ppm	10-40 ppm
Cl	10 ppm	7-11 ppm	10 ppm
Co	10-13 ppm	10 ppm	10 ppm
Cu	10 ppm	25-44 ppm	25 ppm
Hf	52-53 ppm	80-84 ppm	51-57 ppm
Mn	10 ppm	25 ppm	25 ppm
Mg	10 ppm	10 ppm	10 ppm
Mo	20 ppm	25 ppm	25 ppm
Pb	NR	25 ppm	NR
Si	52-54 ppm	60-85 ppm	99-119 ppm
Nb	50 ppm	50 ppm	NR
Ta	100 ppm	100 ppm	NR
Ti	18-48 ppm	25 ppm	25 ppm
U	0.5 ppm	1.8 ppm	1.8 ppm
U235	.002-.004 ppm	.010 ppm	NR
V	20 ppm	25 ppm	NR
W	50 ppm	50 ppm	50 ppm
Zn	50 ppm	NR	NR
H	2-18 (12-17) ppm	5-7 ppm	(12) ppm
N	35-40 (35-43) ppm	40 ppm	(21-23) ppm
O	1100-1140 (1100-1200) ppm	1200-1400 ppm	(1350-1440) ppm

Values reported typically represent the range of analyses determined from various positions on the ingot.

Values in parentheses represent the range of analyses as determined on TREX.

NR = not reported

TABLE VII

AS PILGERED ZIRCALOY-2 TUBING
932°F, 1500 PSI, 24 HOUR EXPOSURE
CORROSION TEST RESULTS

Estimated Approximate Maximum Surface Temp.	Weight Gain (mg/dm^2) $\bar{X}$	Weight Gain (mg/dm^2) S	Remarks
1170-1185°C	52.9	14.7	Adherent black continuous oxide on OD and ID
1210-1275°C	50.6	2.9	Adherent black continuous oxide on OD and ID
1300-1320°C	65.6	5.4	Adherent black continuous oxide on OD and ID
Zircaloy-2 Standards	261.4	51.9	White spalling oxide at edges of coupons

8. A process for improving the high temperature steam corrosion resistance of alpha zirconium alloy bodies which comprises beta treating a first layer of said body, characterized by said first layer is beneath and adjacent to a first surface of said body, and characterized in that said beta treating produces two dimensional linear arrays of precipitates in said first layer; forming a second layer of alpha recrystallized grains beneath said first layer; and then cold working said body.

9. A process according to claim 8, characterized in that the cold working step comprises two or more cold working steps separated by an intermediate annealing step.

10. A process according to claim 8 or 9, characterized in that the two dimensional linear arrays of precipitates are removed.

11. A process according to claim 10, characterized in that the removing step comprises cold working the body to a degree sufficient to redistribute said two dimensional arrays of precipitates in a substantially random manner.

12. A process according to any of claims 8 to 11, characterized in that the beta treating comprises rapidly heating at least a portion of the body to a temperature above the alpha + beta to beta transus temperature.

13. A process according to claim 12, characterized in that a high energy beam is used for the rapid heating.

14. A process according to claim 13, characterized in that the high energy beam is a laser beam.

15. A process according to claim 12, 13 or 14, characterized in that the temperature of the portion of the body is above the alpha + beta to beta transus temperature for a fraction of a second.

16. The process according to any of claims 8 to 15, characterized in that after the last cold working step the body is annealed.

26. An alloy body according to any of claims 20 to 25, characterized in that the alpha zirconium alloy is Zircaloy-2, Zircaloy-4 or a zirconium-niobium alloy.

27. An alpha zirconium intermediate size product characterized in that said product comprises a first integral microstructural layer adjacent and beneath a first surface of said body; a second integral microstructural layer beneath said first layer; said first layer having a Widmanstatten type microstructure; and said second layer having polygonal substantially equiaxed alpha grains and a substantially random precipitate distribution.

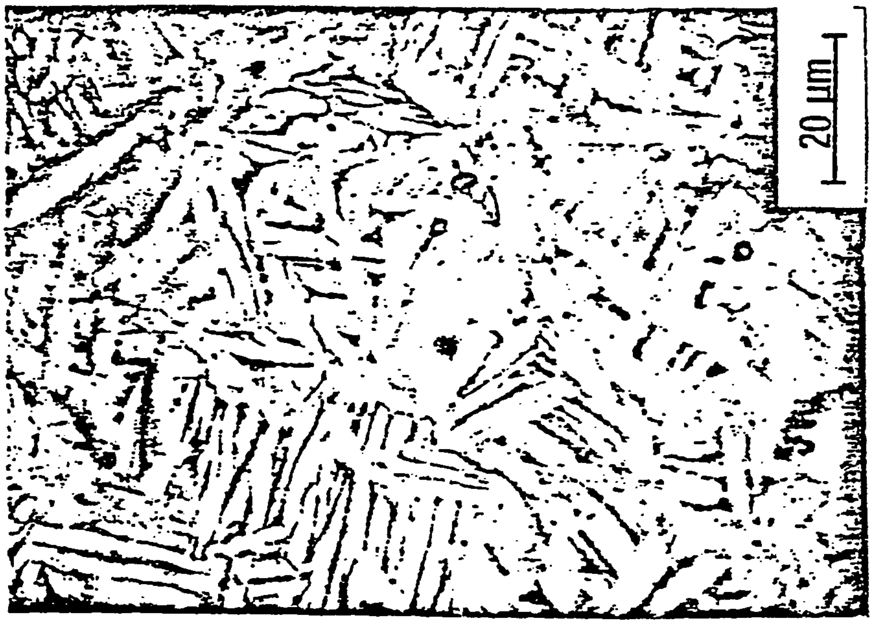

FIG. 3B

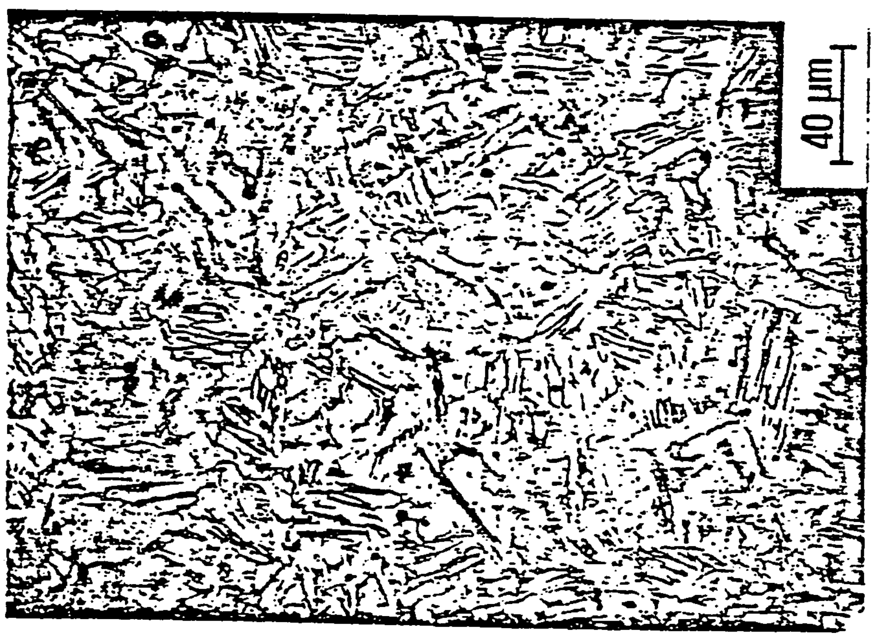

FIG. 3A

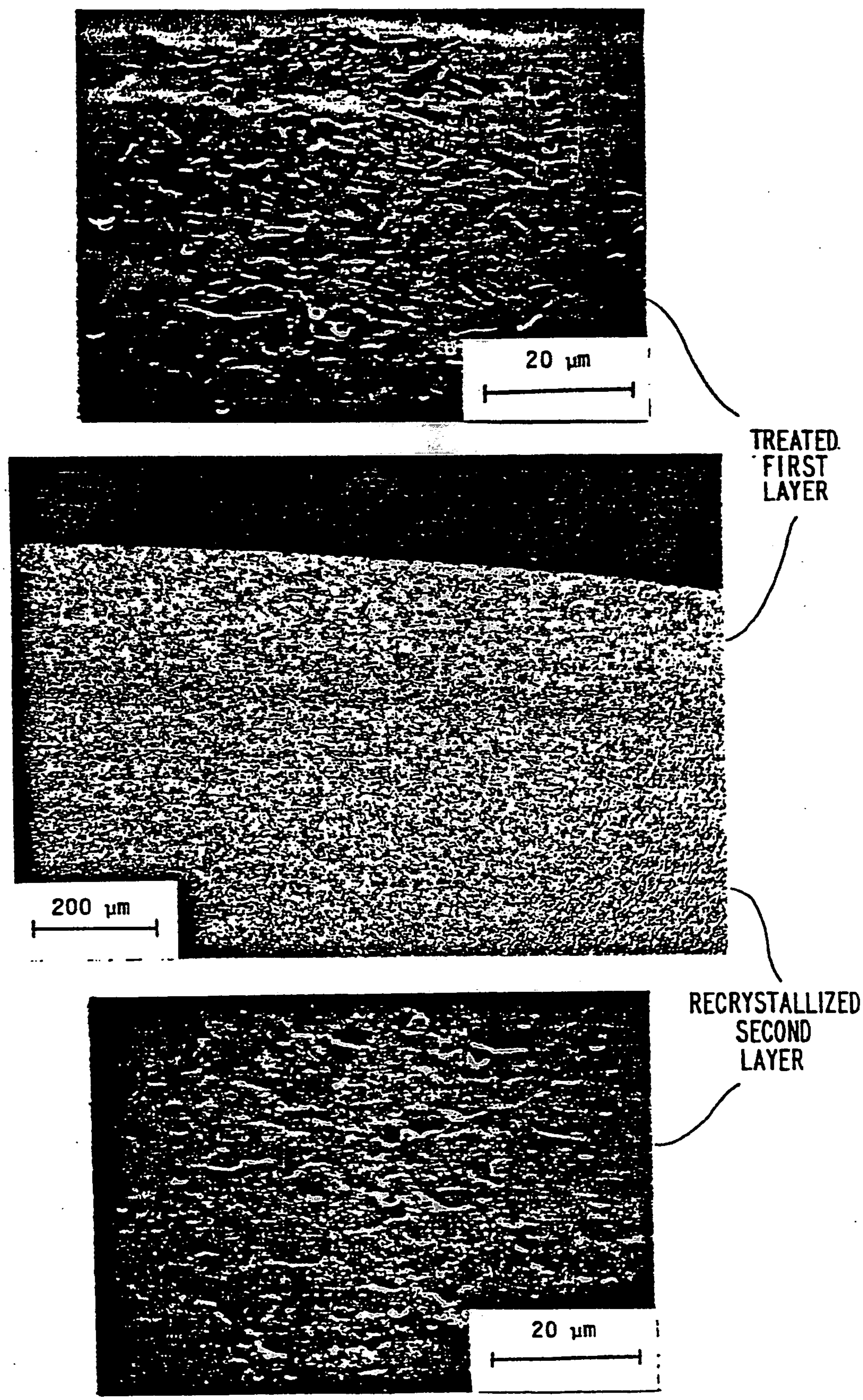
20 µm
TREATED FIRST LAYER
200 µm
RECRYSTALLIZED SECOND LAYER
20 µm

FIG.5

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EUROPEAN SEARCH REPORT

0085552

Application number

EP 83 30 0454

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	US-A-4 294 631 (ANTHONY et al.) * Claims 1,6,7 *	1,5,7	C 22 F 1/18 C 22 F 3/00
X,D	US-A-4 279 667 (ANTHONY et al.) * Claims 1,5,6 *	1,5,7	
Y	FR-A-2 341 665 (UNITED TECHNOLOGIES CORPORATION) * Claims 1,4; page 7, lines 20-29 *	1	
Y	FR-A-2 393 075 (WESTERN ELECTRIC CY) * Claims 1,3 *	1	
A,D	US-A-3 865 635 (HOFVENSTAM et al.) * Claims 1-4 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 3) C 22 F 1/18 C 22 F 3/00 C 22 C 16/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	04-05-1983	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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& : member of the same patent family, corresponding document